

CATALYTIC TWO-STAGE HYDROCRACKING OF ARABIAN VACUUM RESIDUE
AT A HIGHER CONVERSION LEVEL WITHOUT SLUDGE FORMATION

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ABSTRACT

Catalytic two-stage hydrocracking of Arabian vacuum residue was studied using commercial Ni-Mo catalysts in the autoclave to achieve a higher conversion above 50 % into 540 °C⁻ distillate without producing sludge in the product. The hydrogenation at 390 °C of the first stage was found very effective to suppress the sludge formation in the second stage of higher temperature, 430 °C, where the cracking to produce the distillate dominantly proceeded. The catalyst for the residues(KFR-10) was suitable for these purposes, while KF-842 catalyst, which exhibited excellent performance against coal liquid residues, failed to suppress the sludge formation. The shorter contact time of the second stage at a relatively higher temperature appears favorable to increase the conversion without producing the sludge. The mechanism of sludge formation in the hydrocracking process is rather comprehensibly discussed based on the previous and present results.

INTRODUCTION

Demand for clean distillate from the bottom of the barrel leads to severe hydrocracking of petroleum residues at higher temperatures[1]. The severe conditions cause problems of coke deposition on the catalyst and sludge formation in the product oil[2]. Such trouble makers of both carbonaceous materials, of which formation may be intimately related, shorten the life of the catalyst, plug transfer line and deteriorate the quality of the products[3].

Empirically, the dry sludge is believed to be produced when the conversion to the distillate is beyond a certain level(ca. 50 %) regardless of the catalyst and feedstocks[1]. Its structure, properties and formation mechanism are not fully understood yet[4].

In a previous study[5], dry sludge produced in a hydrocracked oil was analyzed chemically, and its solubility, fusibility and reactivity were studied to propose a mechanism of sludge formation in the hydrocracking process.

In the present study, catalytic two-stage hydrocracking was proposed to achieve a higher conversion into 540 °C⁻ distillate above 50 % with a minimum amount of dry sludge in the product. The idea is based on the mechanism previously proposed: the deep hydrogenation of aromatic fraction in the residue by the first stage of lower temperature may accelerate the cracking and solubility of the heaviest aromatic portion in the second stage of higher temperature, where major hydrocracking takes place.

EXPERIMENTAL

Materials

A vacuum residue (b.p. > 550 °C) of Arabian-light oil (10 g), of which properties were shown in Table 1, was hydrocracked by the single- and two-stage reactions under hydrogen pressure (15 MPa), using one of the Ni-Mo catalysts (1 g) in a batch autoclave of 100 ml capacity. The catalysts, of which properties were summarized in Table 2, were presulfided under 5 % H₂S/H₂ flow at 360 °C for 6 h.

Catalytic hydrocracking

The standard conditions were 390 °C-4 h, 420 °C-4 h for the single-stage reaction, and 390 °C-3 h (first stage) and 420 - 440 °C-1 h (second stage) for the two-stage reaction, respectively. No solvent was used except for the two-stage reaction of 390 °C-3 h and 440 °C-1 h; 10 wt% of 1-methylnaphthalene was added before the second stage for comparison with no-solvent reaction under the same conditions. After removal of the catalyst, the product was observed under a optical microscope to measure the amount of sludge in the product. The product was distilled under vacuum (5 mmHg) at 340 °C to obtain the distillate (540 °C fraction) yield.

RESULTS

Single-stage hydrocracking

Table 3 summarizes the results of single-stage hydrocracking using two Ni-Mo catalysts. The reaction at 390 °C provided the yield of 540 °C distillate below 50 %. No sludge was found with both catalysts at this temperature as shown in Figure 1a, where bluish spots of probably long-chain paraffins were observable, indicating insufficient extent of cracking. It is noted that the amount of asphaltene was unchanged after the hydrocracking at 390 °C.

Higher reaction temperature of 420 °C increased the distillate yield significantly above 70 %. However, a large amount of sludges was found with both catalysts as shown in Figures 1b and 1c. The appearances of the sludges were somewhat different with the catalysts; those with KF-842 consisted of black and rigid spheres and very fine brown oily-droplets, whereas those with KFR-10 were larger droplets which were brown and diffused. A significant amount of asphaltene was certainly converted under the conditions. It should be noted that KF-842 produced a significant amount of gaseous products at 420 °C. Thus, the catalysts, KF-842 for the distillate of coal liquid and KFR-10 for the petroleum straight residue behaved very differently against the petroleum residue.

Two-stage hydrocracking

Results of two-stage hydrocracking are summarized in Table 4. The two-stage hydrocracking using KF-842 at 390 °C-3 h and 420 °C-1 h still produced a very large amount of sludge in the product oil as shown in Figure 2a, although the distillate yield was still high. KFR-10 catalyst under the same conditions produced negligible amount of sludge as shown in Figure 2b at the distillate yield as high as 66 %. Longer reaction time of 3 h in

the second stage at 420°C increased slightly both sludge and the distillate yield(70 %).

Higher temperature of 440 °C for 1 h in the second stage increased the yield to 81 %, some sludgebeing produced as shown in Figure 2c.

Addition of 10 % 1-methylnaphthalene to the second stage at 440 °C was very effective to suppress the sludge formation (Figure 2d). The distillate yield was as high as 80 %.

Storage stability of hydrocracked product

The hydrocracked product obtained by the single stage of 420 °C-4 h using KF-842 catalyst was rather unstable. The product carried a small amount of sludge just after the reaction as shown in Figure 1b, however a much larger amount was found 150 days later in the same product(Figure 3). Insufficient hydrogenation or dehydrogenation because of high reaction temperature may leave unsaturated sites reactive for the air-oxidation. In contrast, no deterioration was observed with the products obtained by using KFR-10 catalyst under the same conditions and the two-stage reactions with either catalyst, although a large amount of sludge has been produced right after the two-stage hydrocracking with KF-842 catalyst.

DISCUSSIONS

Structure and formation mechanism of dry sludge in the hydro-cracking

The hexane-soluble fraction (HS) in the hydrocracked product consists of essentially of long-chain paraffins and long alkyl-benzenes. In contrast, the insoluble substances in the sludge are fairly aromatic with much less and shorter alkyl groups and rather polar, carrying a considerable amount of heteroatoms. The solubility decreased with increasing aromaticity and polarity, the molecular weight varying rather slightly among the fractions. Such contrast structural characteristics of HS and HI fractions may not allow their mutual miscibility, precipitating or segregating the insoluble substances from the HS matrix at room temperature.

In spite of low solubilities of the sludge components at room temperature, they melt or are dissolved in the light component at elevated temperatures above 80 °C. Thus, the sludge may disappear at elevated temperatures such as the reaction temperature, although its limited solubility in the matrix may enhance its adsorption or longer residence on the catalyst surface, leading to the severe catalyst deactivation.

Based on the analyses of the sludge, a mechanism of its formation is proposed[5]. Hydrocracking at higher temperatures to achieve a higher conversion can crack deeply the paraffinic and and alkyl aromatic hydrocarbons at a high level, however highly-condensed aromatic hydrocarbons are not fully hydrogenated at higher temperatures for their cracking because dehydrogenation is so rapid under the conditions, staying unchanged in their ring structure to be insoluble in the paraffin-rich matrix, especially at lower lower temperatures. Elimination of alkyl side-chains from aromatic hydrocarbons and severe cracking of light aromatic

hydrocarbons enhance the phase separation to lead to the sludge formation.

Such a mechanism originating from the phase separation of the fractions due to their mismatched compatibility appears to be common to bottom and shot cokes formation in the coking[6,7], and least cracking reactivity of paraffin[8-10] and sludge formation due to the slight oxidation in the coal liquid.

Effects of two-stage hydrocracking

The two-stage hydrocracking which consists of sufficient hydrogenation at a lower temperature and extensive cracking of the hydrogenated product at a higher temperature was found to allow a high yield of distillate over 60 % with a minimum amount of sludge droplets in the product at room temperature. As discussed in the mechanism section, the sludge was unhydrogenated aromatics due to high reaction temperature, which are not miscible with the paraffin-dominant matrix. The first stage of low temperature sufficiently hydrogenates the aromatic parts of the asphaltene to be easily cracked and/or to stay miscible with the matrix, increasing the yield of distillate without producing sludge in the second stage. Aromatic solvent of moderate size such as 1-methylnaphthalene is very effective in the second stage of the short reaction time to suppress the sludge by dissolving the asphaltene.

The selection of conditions for the second stage is very important because extensive cracking should take place before the dehydrogenation. Longer reaction time at higher temperature tends to produce more sludge because uncracked remaining asphaltene in the product becomes sludge. The rapid heating to the temperature of the second stage may be favorable.

The selection of the catalyst is also important. The catalyst should have strong hydrogenation activity against the asphaltene of large molecules. The large pores of the support can get access to such molecules. The catalyst of the second stage should have high cracking activity against the hydrogenated asphaltene without dehydrogenation.

Such a set of the catalysts should be designed separately to exhibit the optimum performances of the respective objectives at the respective stages.

Finally, the stability of hydrocracked product is concerned. The post-hydrogenation may be effective at a lower temperature, where sufficient hydrogenation of the whole product can proceed. Sludge can be completely removed by the steps as described in a previous paper[5]. Short reaction time of the second stage can maintain the hydrogenation level high which is achieved in the first stage, proving the stability of the product.

References

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Table 1

Solubility¹⁾ of Arabian-light vacuum residue (ALVR)

	wt%		
	HS	HI-BS	BI
ALVR	91	9	0

1) HS: hexane soluble

HI-BS: hexane insoluble-benzene insoluble

BI: benzene insoluble

Table 2

Some properties of the catalysts¹⁾

Catalyst name	Support	Metal(wt%)		Surface area (m ² /g)	Pore volume (ml/g)	Mean pore diameter (Å)
		NiO	MoO ₃			
KF-842	alumina	3.1	15	273	0.52	< 100
KFR-10	silica-alumina	1.0	5.0	147	0.71	168

1) Supplier: Nippon Ketjen Co.

Table 3

Catalytic performances in the single-stage hydrocracking of ALVR

Catalyst	Conditions (°C- h)	Recovery (wt%)	D.Y. ¹⁾ (%)	A.S. ²⁾
KF-842	390-4	95	39	tr.
	420-4	75	72	much
KFR-10	390-4	98	41	tr.
	420-4	91	74	much

1) D.Y.: 540 °C⁻ distillate yield

2) A.S.: Amount of sludge, tr.: trace

Table 4

Catalytic performances in the two-stage hydrocracking of ALVR

Catalyst	Conditions (°C- h)	Recovery (wt%)	D.Y. ¹⁾ (%)	A.S. ²⁾
KF-842	390-3			
	420-1	94	63	much
KFR-10	390-3			
	420-1	94	66	v.tr.
	390-3			
	420-3	94	70	tr.
	390-3			
	440-1	93	81	some
	390-3			
	440-1 ³⁾	95	81	v.tr.

1) and 2): See Table 3., v.tr.: very trace

3) 10 wt% of 1-methylnaphthalene was added prior to the second stage.

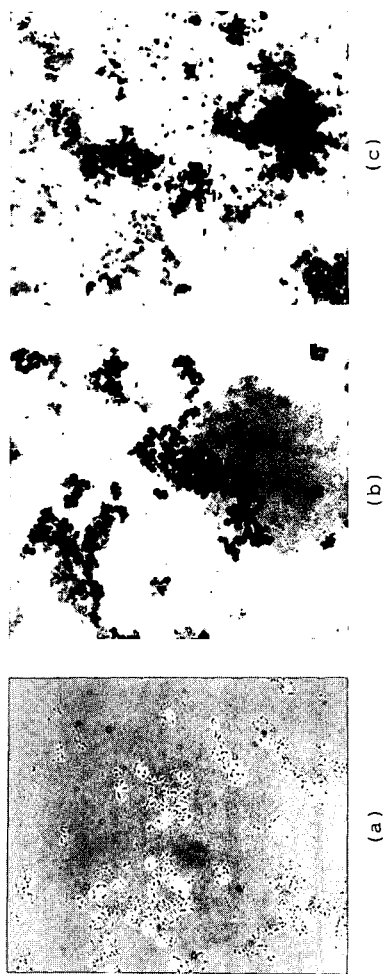
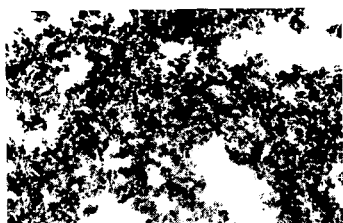
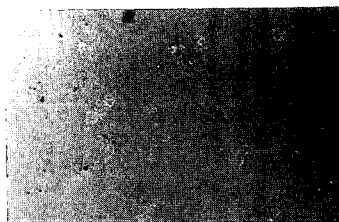


Figure 1 Microphotographs of the product oil in the single-stage reactions

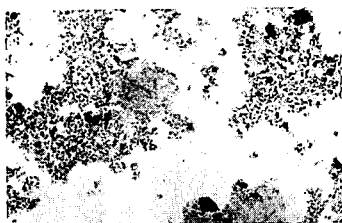
- (a) 390 °C-4 h (either catalyst)
- (b) 420 °C-4 h (KF-842 catalyst)
- (c) 420 °C-4 h (WFR-10 catalyst)



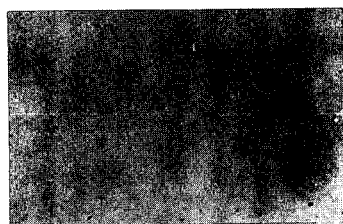
(a)



(b)



(c)



(d)

Figure 2 Microphotographs of the product oil in the two-stage reaction
 (a) 390 °C-3 h and 420 °C-1 h (KF-842 catalyst)
 (b) 390 °C-3 h and 420 °C-1 h (KFR-10 catalyst)
 (c), (d): 390 °C-3 h and 440 °C-1 h (KFR-10 catalyst)
 (c) no solvent added
 (d) 10 wt% of 1-methylnaphthalene added in the second-stage reaction

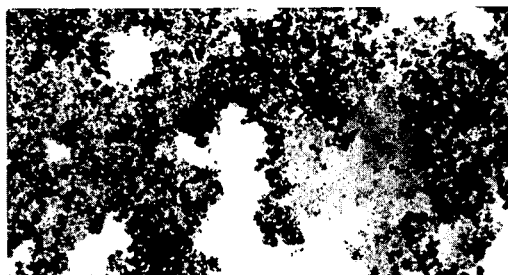


Figure 3 Microphotographs of the product of 420 °C- 4 h (KF-842) after 150 days